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A Systematic Separation of the Acids of Group 1

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A SYSTEMATIC SEPARATION OF THE ACIDS OF GROUP 1

BY

HERBERT AUGUST WINKELMANN
B. S. Northwestern College, 1914

THESIS

Submitted in Partial Fulfillment of the Requirements for the

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

HERBERT AUGUST WINKELMANN

ENTITLED A SYSTEMATIC SEPARATION OF THE ACIDS OF GROUP I.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE, in Chemistry

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A SYSTEMATIC SEPARATION
# of the
ACIDS OF GROUP I

I. INTRODUCTION

Very little work has been done upon a systematic separation of the acids. The customary methods for the recognition of the various acids depend mainly upon the various group reactions, followed by specific tests for one or the other anion, and a process of elimination. In a few cases, special methods have been worked out for the separation of certain commonly occuring mixtures, such for instance as the three halogens, and some of the anions of sulphur, but on the whole, little regard has been paid to complications arising when a number of acids are present at once. The errors and confusion resulting from the customary method of attack, become particularly pronounced in the case of students first confronted with the problems of recognizing and distinguishing between the various negative radicals in an unknown mixture. While they obtain a fairly comprehensive view of the relations between the metallic elements in their reactions, this is not true of the non-metallic elements. As an actual fact, the student is just as likely to be confronted at some latter time with a mixture of various acid radicals as with a substance containing a number of metals.

The only work recently published with a view to a fairly comprehensive scheme of separation is that of A. A. Noyes.[*]

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[*] Jo. Amer. Chem. Soc. 34 609 (1912)

The fundamental idea of this method is the separation of the volatile and non-volatile acids in various stages by distillation after addition of phosphoric acid. The more volatile acids, such as hydrocyanic acid, are collected in the first distillate, the less volatile in the second. The various portions are then examined much in the customary manner, for specific reactions of one or the other acid, without attempting to effect a furthur separation. The method is, in many respects, ideal and very effective, and a very great improvement upon the somewhat haphazard procedures previously described. In cases in which the nature of the mixture is such that interaction between the various constituents is possible, the prolonged heating during distillation will hasten and extend decomposition with resulting decrease of directness or certainty in the results. The fact that each distillation with phosphoric acid entails destruction of the distillation flask does not involve more than a slight inconvenience in individual cases; where the method is, however,to be applied repeatedly by large numbers of students, this factor does become one which it is desirable to eliminate.

The part of the investigation presented here has to do with the first group of acids, in the following classification,

I. Anions which give a silver salt insoluble in dilute nitric acid, but whose barium salts are soluble in water or acids.

II. Anions which give a silver salt difficultly soluble in neutral solution, but readily soluble in dilute nitric acid, and whose barium salts are readily soluble.

III. Anions which give silver and barium salts insoluble in water alone, but soluble in the presence of dilute nitric acid.

IV. Anions which give salts of silver and barium readily soluble under all conditions.

V. Anions which give silver salts soluble in water, but whose barium salts are insoluble, even in the presence of nitric acid.

The anions included in this first group are Cl^-; Br^-; I^-; CN^-; CNS^-; $Fe(CN)_6^{III}$; $Fe(CN)_6^{IV}$; $S^{=}$.

The first task was the collection of the solubility data of the anions combined with metals,in alkalies, acids, or other salts; and an examination of those cases which offered promise of being serviceable. In the cases of some of the anions, it was easy to find insoluble salts, but difficult to effect a separation, due to similar properties of some of the anions. Other anions give but few insoluble salts, and of these, a still smaller number were adapted to the purpose in view. In many cases, the data given as authentic in the literature, were obtained under ideal conditions, and hence were inapplicable to the present case; thus necessitating a determination of limits of sensibility for every step taken, since the effects of the various anions upon each other were unknown.

All of the acids can be separated in different ways on the basis of the solubility of their various salts except in the case of the cyanide, and thiocyanate. These two anions only, yield several insoluble salts. In the literature, nickel and cobalt cyanide are given as insoluble, and the thiocyanates as soluble. These results were obtained under ideal conditions; that is, referred to pure water. But in solutions such as these, dealt with in this separation, where either acid or alkali is always present, it was found impossible to separate the insoluble cyanide from the soluble thiocyanate by using either cobalt or Nickel.

The effect of the complications introduced in the course of analysis is shown by the results tabulated under these and various other metals furthur on.

II. SEPARATION OF FERROCYANIDES AND FERRICYANIDES.

The plan which first suggested itself was to add metallic zinc to the mixture of the silver salts of the acids. The silver salts are thus reduced with the production of metallic silver and the corresponding zinc salts. The zinc ferrocyanide and ferricyanide being insoluble, will remain with the reduced silver and unused zinc; the remaining zinc salts are left in solution. This method was not at all neat and it lost in sensitiveness as a result of the occlusion of some of the other anions by the metallic silver or zinc. In addition, as shown by G. McP. Smith,* metallic zinc, when acting on potassium ferricyanide will reduce the same, and also give the ferrocyanide in the solution. None of the zinc, however, was found in the filtrate. This was the reason for some of our erroneous results, namely, that of finding ferrocyanide, when none was originally present.

This proceedure would have been more in harmony with the steps to be anticipated in the succeeding groups, since the first groups could there be removed as a whole. It was , however, not found feasible to carry it out in this manner. The difficulty was obviated by adding zinc nitrate to the solution before adding any

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* Zeit. fur Anorg. Chem. 82 65 (1913)

silver nitrate. The insoluble zinc ferrocyanide and ferricyanide are precipitated, leaving the remaining acids of the first group in solution, from which they are precipitated by silver nitrate. Experiments performed to determine the sentiveness of this method showed that in a solution containing dilute nitric acid, 0.05 mgs. of ferricyanide or ferrocyanide in ten cc. total volume gave a decided precipitate, while 0.02 mgs. could still be dectected by an experienced observer. The separation of the two zinc salts was found to be readily effected by means of ammonium hydroxide, and will be described under the general procedure. Another treatment is with socium hydroxide and ammonium nitrate, which will also be taken up later on.

III.SEPARATION OF THE REMAINING ANIONS.

Having precipitated the silver compounds of Cl^-, Br^-, I^-, CN^-, CNS^-, $Fe(CN)_6^{\overset{\equiv}{-}}$, $Fe(CN)_6^{\overset{=}{-}}$, and $S^=$, the next step was to determine upon a process of separation and identification. A brief description of some of the processes tried, and the reason for rejecting various ones will follow.

A. Ammonium Hydroxide.

Since ammonium hydroxide is a good solvent for some silver salts, the possibility of its use for the separation was examined. Silver iodide and sulphide were found to be insoluble under all conditions. The solubility of the silver salts under examination, differed considerably under varying conditions, which made a separation by this method not feasible. For example, silver chloride is easily soluble in dilute ammonium hydroxide, whereas the

bromide is but slightly so, but easily soluble in concentrated. The thiocyanate is soluble only in concentrated ammonia. The ammonium cyanide is also very unstable, so that even if a separation is obtained, there is danger of decomposition in subsequent manipulations.

One of the fundamental objections to this method is the unreliability of the results obtained, in attempting to extract a more soluble substance from an admixture containing less soluble substances. This is never possible with mathematical precision, and, unless the differences in solibility are very great, it is not even possible for practical purposes. Given large quantities of two such constituents, for instance, silver bromide and silver iodide, such a method gives decided results. But at the extremes of the range of mixtures, the results are of necessity erroneous. Thus a large quantity of iodide will prevent solution of small percentages of bromides, and conversely, small percentages of iodide will dissolve with the larger portion of bromide. Methods of separating the silver halides by ammonia do not seem to have obtained wide application, although several have been described.

For these reasone, the method was abandoned after a brief examination of its possibilities.

B. Lead Salts.

The behavior of the lead salts of this group of acids was then studidd, in an effort to see if iodine might be separated as lead iodide, after the reduction of the silver salts. The following table shows the behavior of lead acetate added to a neutral solution of the anions, and in acid solution of the anions.

Behavior of Lead Acetate with various salts (vol. 10 cc.)

added to a neutral solution of:

	1mg.	3mg.	5mg.	7mg.	10mg.	Solution acid (1-2 cc.dil.HNO_3) 1mg.	3mg.	5mg.	7mg.	10mg.
KCl--	+	+	+	+	+	–	–	–	–	–
KBr--	+	+	+	+	+	–	–	–	–	–
KI---	+	+	+	+	+	–	–	–	+	+
KCN--	+	+	+	+	+	–	–	–	–	–
KCNS-	+	+	+	+	+	–	–	–	–	–

The results given in the above table show that this salt does not offer a satisfactory means of separation, since in neutral solutions a precipitate was obtained in every case, while in an acid solution, 7 mgs. of iodide yielded only a slight precipitate and ten mgs. only a fair one. Even if the lead iodide separation had been practicable, the lead would again have to be removed after proceeding with another step. Such an extra step increases the liability of losing small amounts of the acid, and is an added disadvantage in the use of lead.

C. Mercurous Salts.

Another plan tried was to add mercurous nitrate to the acidified solution containing the anions under discussion. The mercurous cyanide, thiocyanate and iodide are soluble in excess of the mercurous nitrate, or in nitric acid, while the bromide and chloride are insoluble.

Behavior of Mercurous nitrate. (Vol. 10 cc.)

	3 mg.	2 mg.	1 mg.
KCl ----------	+	+	+
KBr ----------	+	+	+

KI ----Yellow ppt. dissolves immediately in excess $HgNO_3$ or HNO_3.

KCN ----White ppt. " " " " " " "

KCNS----White ppt. " " " " " " "

The chloride and bromide being insoluble, the action of mercurous nitrate upon the silver salts of these two anions was studied.

Behavior of mercurous nitrate upon silver chloride and bromide.

	$AgNO_3$	$HgNO_3$
KCl ------	ppt.	ppt.
KBr ------	"	"
KI ------	"	solution
KCN ------	"	blackens, solution
KCNS -----	"	solution

The chloride and bromide were each treated with ammonium hydroxide to determine if the mercurous chloride and bromide had really been formed. The white precipitates both blackened, showing the presence of the mercurous salts. The first objection to the scheme came when it was found that part of the chloride and bromide were also in solution, which is just what was not desired.

The plan was finally rejected because in using mercurous nitrate, the mercury would have to be removed before trying to detect for any other anion. This would necessitate the introduction of hydrogen sulfide or sodium chloride. The cyanide was invariably lost in this procedure, when present in small quantities. The plan of reprecipitating and redissolving the precipitate in excess was not at all practical in this case, and was abandoned after the study of the formate reduction and cuprous salts had been investigated.

D. Formate Reduction.

Since zinc was found not to be a very satisfactory reducing agent, and after reduction, a separation was impossible to find, other reducing agents were examined. Sodium formate was then

studied, as was also formaldehyde and formic acid. Freshly precipitated salts were washed free from traces of free silver. A few drops of ammonium hydroxide were added, and six to ten drops of normal potassium hydroxide, and then 0.5-2 grams of sodium formate or several cc. of formaldehyde and formic acid. Theoretically, one gram of sodium formate should reduce two grams of silver chloride, consequently only a small amount of reducing agent is necessary. The ammonium hydroxide is used because it hastens the solution of the silver salts. Reduction was carried out by heating, the total volume being kept as near ten cc. as possible. The following table shows the results obtained by using the three reducing agents, from which interesting conclusions can be drawn.

Action of Reducing Agents on Silver Salts. (Time 15-30 min.)

Compound taken. 5 mgs.	Formaldehyde.	Formic acid.	Sodium Formate in presence of KOH.
AgCl	+	+(rapid red)	+
AgBr	+	+(slower)	+
AgI	+	–	–
AgCN	–	+	+
AgCNS	+	+(slow red)	+
$Ag_3Fe(CN)_6$	+	+(poor test)	uncertain. no test.
$Ag_4Fe(CN)_6$	+	+(poor test)	– (decomp.)
AgS	–	–	–

It was at first thought that the formate reduction could be applied directly to a precipitate containing also the ferrocyanides and ferricyanides in order to find out whether the precipitation of zinc ferrocyanide and ferricyanide at the outset of the analysis could be dispensed with. This would possibly have been more

satisfactory as far as manipulations in the suceeding groups are concerned. However, no reaction for ferrocyanide or ferricyanide could be obtained in the filtrate from the reduced silver.

Upon examining the precipitate, it was found that the two complex cyanides had decomposed, if not altogether, at least partially.

Acidifying the precipitate from the ferricyanide with sulphuric acid, and adding potassium thiocyanate proved the presence of ferric iron. Adding potassium ferricyanide to the precipitate from the ferrocyanide, and acidifying, showed the presence of ferrous iron. The breaking up of the complex anion would introduce cyanide into the solution, and would make it impossible to decide whether tests for original cyanide were valid. The necessity of removing the ferrocyanides and ferricyanides with zinc nitrate before separating the other groups by the silver precipitation still remained.

As is seen in the table, neither the iodide nor sulfide were found in the filtrate of the sodium formate reduction. This was carefully studied and in not a single case, has a trace of iodine been found in the filtrate. Five mgs. of silver iodide were boiled for one hour with sodium formate, without a trace of iodine in the filtrate, whereas all the other silver salts were completely reduced in 15-30 minutes of energetic boiling, even in mixtures containing varying quantities of each.

To prevent loss of the cyanide during boiling, and to hasten the reduction, a little caustic alkali must be added, enough to give a distinct alkaline reaction is sufficient. Under these conditions, the solution may be boiled or evaporated without mater-

ial loss of hydrocyanic acid.

The precipitate was then examined for iodide and sulfide, by reducing with metallic in neutral solution. The iodide was always found to be present in this filtrate. Upon acidifying the precipitate with hydrochloric acid, the sulfide was evolved as hydrogen sulfide.

The sodium formate reduction has proven to be the most satisfactory reducing agent; and not only that, but it has aided in the separation of two otherwise difficultly separable anions.

E. Cuprous Salts.

The behavior of cuprous salts was next investigated while trying to separate the chloride, bromide, cyanide and thiocyanate from one another. The precipitation of copper as the thiocyanate is a well known quantitative method. It remained to be seen how the other ions present would distribute themselves, particularly when one orthe other was present in large quantities. It was found that in the presence of sulphurous acid, cuprous chloride and bromide remain in solution, whereas the cyanide and thiocyanate will precipitate.

Behavior of Cuprous Salts in Presence of SO_2 (10 cc.).

KCl	100 mg.	soluble
KBr	100 mg.	"
KCN	100 mg.	precipitates
KCNS	100 mg.	"

While working on this method, a paper by L. J. Curtman and A. G. Wickoff[*] on the same salts appeared which confirmed the re-

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[*] Jo. Amer. Chem. Soc. 37 298 (1915)

sults we had obtained. This paper called attention to the interference of cyanides, thiocyanates and ferricyanides in the detection of bromides by ordinary methods, and the determination of this interference. They found that they could detect two milligrams of bromine in the presence of 500 milligrams of the interfering substances.

When the thiocyanate and cyanide are precipitated, the chloride and bromide could be detected, but the matter of treating the precipitate presented a difficult problem. The most difficult problem of the whole procedure has been the separation of this precipitate. Various salts such as ammonium chloride, ammonium sulfate,sodium thiosulfate, nitric acid were tried in order to find one which should dissolve only one of the two, but without success.

Finally the following procedure was adopted; a few drops of normal potassium hydroxide were added to the precipitate and diluted with 3-4 cc. of water and heated gently, and then diluted to ten cc. The cuprous salts are decomposed giving a precipitate of cuprous oxide, while the cyanide and thiocyanate pass into solution. The cuprous oxide is filtered off, and the filtrate is treated for cyanide and thiocyanate. It was found necessary to remove the copper completely before the test for the presence of cyanide could be made. Its presence interferes with the conversion of the cyanide into the ferric ferrocyanide or Prussian blue. When copper was present in a known amount of cyanide, instead of Prussian blue, a red precipitate which was probably $Cu_2Fe(CN)_6$ was formed. This seemed to be formed in a small amount compared to the amount of cyanide present. It is quite essential to remove the copper, but a large excess of alkali should be avoided so as

not to dissolve any of the copper.

For increasing the sensitiveness of the ferrocyanide reaction, the addition of potassium fluoride as advised by A. Vichoeuer and C. O. Johns[*] was used. It must be noted however, in this connection that the sensitiveness of the reaction for potassium thiocyanate, which is to be determined in the same solution, is destroyed. Thus a red ferric thiocyanate solution can be completely bleached by sufficient potassium fluoride. The action of potassium oxalate and phosphate was tried, but they had no effect like the fluoride. Since the delicacy is increased in a platinum dish as well as in a glass tube, the reaction cannot be solely based upon the formation of a fluosilicate, although the action on a test tube would lead one to think that the formation of the fluosilicate was an important factor.

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[*] Jo. Amer. Chem. Soc. 37 601-7 (1915)

IV. PROCEDURE.

Precipitation of Ferricyanides and Ferrocyanides.

Procedure I.

Add one to three cc. of dilute nitric acid to a neutralized mixture of acids, and then enough zinc nitrate to insure complete precipitation of the ferricyanide and ferrocyanide. Completeness of the precipitation is indicated by a noticeable change in the character of the precipitate which is colloidal at first but coagulates more readily when excess of precipitant is present. When sufficient ferricyanide is present to color the solution, there is a fairly sharp end point, consisting in the discharge of the yellow color. When not enough zinc nitrate is present, the solutions are colloidal, an excess of zinc nitrate to insure complete precipiattion of the ferricyanide and ferrocyanide being advantageous. 1-2 grams of ammonium nitrate hasten coagulation of the colloidal precipitate. In the complete absence of ammonium salts, the zinc precipitate was found to remain colloidal indefinitely.

Heating of the solution should be avoided, since it increases the tendency of the precipitate to become colloidal, and would cause loss of part or all of the hydrocyanic acid. Ageing seems to favor the separation of the precipitates. Should the precipitate run through the filter, which for this case should be a fairly close grained filter, it should be set aside for a shott period when the precipitate usually will be found to have changed sufficiently to permit satisfactory filtration. The same effect may be obtained more rapidly by shaking the suspended prscipitate ener-

getically in a stoppered flask. This is, in effect, simply the ageing of the colloid and is very effective in producing a precipitate which does not run through the filter.

(a) After washing the zinc precipitate on the filter several times with a few cubic centimeters of a dilute ammonium nitrate solution, (rejecting all but the first washing,) pour ten cc. of a warm 3% NaOH solution through the filter. This sufficient for quantities up to 200 mg. of each of the two salts, which dissolve, yielding the alkali ferri- and ferrocyanide and sodium zincate. Add to the resulting solution 5 cc. of a 5% ammonium nitrate solutionand shake vigorously. The zinc ferrocyanide is precipitated as a gelatinous white precipitate.* This precipitate is quite characteristic. It may, if desired, be furthur characterized by the conversion into the cupric or ferric ferrocyanide. The red cupric ferrocyanide is to be preferred since it is just as sensitive and cannot be confused with the ferrous ferricyanideaas the ferric ferrocyanide may. In either case, the ferrocyanide of zinc is dissolved in a small quantity of NaOH solution, the copper or iron is added and the solution then acidified. This is preferable to acidifying first, particularly when only small quantities are present, since the zinc ferrocyanide when once formed, is not converted into the copper or iron salts very rapidly.

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* The character of this precipitate is particularly well adapted for quantitative approximation. A series of seven precipitates obtained in the regular course of analysis and varying from 100 to 1 mg. in approximately even steps, were correctly estimated by four out of five observers entirely unused to the method.

(b) Another method which was used largely throughout this work, and gave very satisfactory results, was based on the solubility of zinc ferricyanide in ammonium hydroxide. The precipitate of the ferri- and ferrocyanide of zinc is first treated with ammonium hydroxide and then washed. The remaining precipitate, the ferrocyanide, is then dissolved in sodium hydroxide. When the two anions are thus separated, the confirmatory tests following may be applied. This method, while good, has an extra step compared with the previous method. Since in the previous method, the whole precipitate is immediately dissolved in caustic alkali, and the separation then effected by precipitation.

The ferricyanide is identified by acidifying the filtrate from the zinc ferrocyanide (from a) with dilute hydrochloric acid, and adding 1-2 cc. of potassium iodide solution(this should not give free iodine upon acidification), and 0.5-1cc. of $CHCl_3$ or CCl_4. The ferricyanide is reduced, giving free iodine in the $CHCl_3$ layer.

$$2\ K_3Fe(CN)_6 - 2\ KI — 2\ K_4Fe(CN)_6 - I_2$$

A ferric salt gives with a ferrocyanide a blue precipitate of ferric ferrocyanide, but not with ferricyanide. A ferrous salt gives with a ferricyanide a similar blue precipitate of ferric ferrocyanide. It gives with ferrocyanide a white precipitate of ferrous ferrocyanide, when no ferric salt is present, but turns blue in the air. In order to test for the ferricyanide with a ferrous salt the solution must be fresh, that is, free from ferric salt. In using this as a test for the ferricyanide, one is not always sure whether the precipitate may not have been due to a trace of ferric iron, which would give a similar precipitate with ferro-

cyanide . The reaction with potassium iodide is to be preferred for this reason. When applying this test for small quantities, it is necessary to bear in mind that commercial iodides contain usually, traces of iodates and will consequently give traces of free iodine on acidification. A reagent which will not liberate free iodine upon acidification may very conveniently be made by boiling a neutral, or but faintly acid, solution of potassium iodide with metallic magnesium.

The oxidation of iodides by ferricyanides is slow,and in testing for small quantities, time must be given for the iodine to be liberated. As in the case of ferrocyanide,a fairly accurate estimation can be madewhen amounts from 100-1 mg. were used by one unused to this method.

The results obtained during experimentation on the above separation are given in the following tables.

Sensitiveness of test with zinc nitrate in presence of dilute HNO_3. (vol. 10 cc.)

mgs. --------	10	8	6	4	2	0.5	0.1	0.02.
$K_3Fe(CN)_6$ ---	+	+	+	+	+	+	+	+
$K_4Fe(CN)_6$ ---	+	+	+	+	+	+	+	+

Zinc Ferricyanide Reaction. Reliability in presence of the other substances. (vol. 10 cc.)

In Presence of 200 mgs. of:	0.0 mg.	0.1 mg.	0.2 mg.	0.5 mg.	1 mg.
KCl -----------	−	+	+	+	+
KBr -----------	−	+	+	+	+
KI ------------	−	+	+	+	+
KCN -----------	−	+	+	+	+
KCNS ----------	−	+	+	+	+
$K_4Fe(CN)_6$------	−	+	+	+	+

Zinc Ferrocyanide Reaction. Reliability in the Presence of the Other Substances. (vol. 10 cc.)

In presence of 200 mgs. of	0.0	0.1 mg.	0.2 mg.	0.5 mg.	1 mg.
KCl --------	–	+	+	+	+
KBr --------	–	+	+	+	+
KI --------	–	+	+	+	+
KCN --------	–	+	+	+	+
KCNS --------	–	+	+	+	+
$K_3Fe(CN)_6$ ---	–	+	+	+	+

Procedure II.

The filtrate from the zinc precipitation is treated with silver nitrate until precipitation is complete. If cyanides are present a furthur indication of the completeness of precipitation issobtained by the disappearance of the odor of hydrocyanic acid. When a slight excess of silver nitrate has been added, shake the precipitate to coagulate it. Filter or decant and wash twice, collectint the first washing with the filtrate, which contains the acids of the succeeding groups. Wash the precipitate at least three times more, or until no silver is found in the washings.

Procedure III.

Transfer the precipitate to a beaker and add 1-2 grams of sodium formate, (the amount taken will depend on the quantity of precipitate taken, however) . Add three drops of dilute ammonium hydroxide and then 5-10 drops of normal caustic alkali. Add water to make a volume of 10-20 cc., and boil vigorously, keeping the volume the same during the reduction. Reduction is complete when there is no silver left in the solution. The time re-

quired is geherally from 15-30 minutes. When toommuch alkali is used, there is a tendency for the silver to become colloidal, and very difficult to reduce.

Procedure IV.

The solution is filtered off and the precipitate is washed twice, collecting the first washing with the filtrate. The precipitate is transfered to a beaker, and 0.2-0.8 grams of zinc is added. Allow the reduction to take place in neutral solution. If any iodide is present it will pass into solution as zinc iodide and may be identified in the filtrate by several characteristic tests.

(a) Pour off the solution from the zinc reduction, filtering if necessary, also saving the precipitate for procedure five. Acidify with 1-3 drops of dilute acetic acid, and add one to two drops of thallium nitrate. A yellow precipitate of thallium iodide forms, which is quite characteristic of iodine. The following table shows the limits of sensibility with and without intervening reduction.

Behavior of Thallium Nitrate in Presence of Iodide.(vol.10cc

mgs. of KI.	5 mg.	3 mg.	0.5 mg.	0.3 mg.	0.1 mg.	0.05mg
No intervening reduction.						
	+	+	+	+	+	+
With intervening reduction.						
	+	+	+	+	+	+

(b) Another delicate test is the oxidation of the iodide to free iodine by any of the customary methods. The reaction between ferricyanide and an iodide in the presence of an acid has proven very satisfactory. Acidify the filtrate containing the

iodide (from division a) with 1-2 cc, of dilute hydrochloric acid, add 1-2 mgs. of potassium ferricyanide, and 0.5-1 cc. of chloroform or carbon tetrachloride. Shake thoroughly and if any iodide is present, iodine will be liberated. This test has been found sensitive to 0.02 mg.with a good degree of certainty. With small quantities of iodine, the color developes slowly.

The precipitate from division (a) contains the insoluble zinc sulfide. Transfer the precipitate to a test tube with one to two cc. of water, acidifying with 1-3 drops of dilute hydrochloric acid. If any sulfide is present, hydrogen sulfide gas will be evolved, which may be easily confirmed by holding a piece of filter paper saturated with lead acetate over the mouth of the test tube. A black precipitate of lead sulfide will be due to the action of the hydrogen sulfide.

Procedure V.

The clear filtrate from procedure (4) conatining the chloride, bromide, cyanide and thiocyanate is heated to boiling[*]. Any silver in solution will come down, and must be rejected unless the quantity is large in which case it is added to the remainder of the silver reduction. To prevent loss of cyanide, the solution must be kept alkaline all the time. The hot solution is nearly neutralized with dilute sulfuric acid,[* *] and five to fifteen cc. of **saturated** sulphur dioxide solution are added. Then with constant stirring copper sulfate is slowly added until an excess is present. If there is not enough sulfurous acid, the solution may be green,

[*] It is unnecessary to boil the solution.

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[*] If a white precipitate forms here, it is silver, and is present due to the complete reduction with sodium formate and may be rejected.

due to the fact that some of the thiocyanate is still uncombined with the copper. While still hot the solution is filtered. Unless thoroughly coagulated, the precipitate has a tendency to run through the filter, hence a close grained filter is necessary. The precipitate should be washed with hot water, and the first washings collected with the filtrate.

Procedure VI.

The precipitate from procedure (5) contains the cyanide and thiocyanate. Transfer it to a beaker with water, making a volume of ten cc. Add caustic alkali or carbonate to precipitate the copper, allowing the anions to pass into the solution. 1-4 drops of normal potassium hydroxide should be sufficient. A strong solution of alkali would interfere seriously with the delicacy of the cyanide test. If present in fair quantity, say 5 mgs., the cyanide and thiocyanate may be separated by converting the cyanide into Prussian blue and filtering. Adding ferric chloride to the alkaline solution causes Prussian blue to precipitate in flocks at once when acidified, instead of the usual preliminary colloidal form. The red ferric thiocyanate will be in the filtrate, while the Prussian blue will be on the filter. When only small portions of either anion are present, half of the solution must be taken and tested for the presence of each anion. When this is done, potassium fluoride may be used to advantage in testing for cyanide since a separate portion is to be tested for the thiocyanate.

Procedure VII.

The filtrate from procedure (5) contains the chloride and bromide anion. Boil the solution until free from fulfur dioxide until a volume of 5-10 cc. remains. A precipitate forming here may be rejected, since cuprous chloride is quickly hydrolyzed by

hot water to cuprous oxide. Boiling is most conveniently carried on in an Erlenmeyer flask, to insure against loss.

(a) Filter off the cuprous oxide and pour the filtrate into a test tube. Acidify with 1-2 cc. of dilute sulfuric acid and add 1 cc, of 0.1 normal potassium permanganate. After shaking a few seconds, 0.5-1 cc. of carbon tetrachloride is added. Continue the shaking and if a yellow color appears in the tetrachloride, bromine is present.

(b) To test for chloride, draw off the liquid portion from (a), and add from 15 tp 20 cc. of the permanganate solution. If not already sufficiently acid, more sulfuric acid is added. Boil this solution for 5 minutes, or until no furthur bromine comes off, and the volume is down to 10 cc. The manganese dioxide is filtered off, and if the filtrate is pink, a drop of sulfurous acid will destroy the color.Dilute the solution to 50 cc., add 1-2 cc. of dilute nitric acid, and one drop of normal silver nitrate solution. A white precipitate shows the presence of chloride.

(c) Another method of detecting the bromide, without taking the first step of dissolving the oxidized bromine in carbon tetrachloride, is the use of fluorescin paper. In this manner the bromine can be detected at the same time that the complete oxidation of the bromine for the chloride test is taking place. Filter paper, dipped in a concentrated solution of fluorescin in acetic acid is held over the vessel from which the vapor is coming. Traces of bromine are shown by pink streaks, due to the formation of eosin. This method is not applicable for a mixture of free bromine

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A. A. Noyes. Jo.Amer. Chem Soc. 34 639, (1912)

and large amounts of free chlorine. But in a mixture of chloride and bromide, the method is very delicate, and the bromine can be liberated by means of potassium permanganate.

Compt. Rend. 125 654 (1897) Abs. J. C. S. II 138 (1898)

Since any cyanide that might be present is volatilized, and the bromine can all be oxidized, it was thought advisable to find out if the thiocyanate would have any effect upon oxidation with potassium permanganate in case any were in solution. Portions of 20 and 40 mgs. of potassium thiocyanate were treated with 15-20 cc.of potassium permanganate solution, and acidified with 1-2 cc. of dilute sulfuric acid and boiled. The MnO_2 was filtered off and the filtrate was tested with ferric chloride, but without result; also by acidifying some of the filtrate with dilute nitric acid and adding silver nitrate, but no precipitate was formed. The thiocyanate, if any were possibly present, would not interfere with the chloride test, as has also been shown by A. A. Noyes.*

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* Jo. Amer. Chem. Soc. 34 639 (1912)

The general conclusion is that if this test is carefully conducted, it should hold good for chlorides to a very great degree of delicacy in presence of the cyanide, thiocyanate, and bromide, as is shown to be the case.

The following table shows the limits of sensitiveness for each test of an anion, in absence of the others. Each anion was treated through the whole scheme of analysis, in the amounts given at the top of the table. Each analysis was conducted in triplicate and since results checked so closely in most cases, an average,

or only one result, will be tabulated for a given amount of anion.

Sensibility of Each Anion in Absence of Others Carried through the Scheme.

	10 mg.	5 mg.	1 mg.	0.1 mg.	0.01 mg.	0.02 mg.
KCl --------	+	+	+	+	+	−
KBr --------	+	+	+	+	+	−
KI ---------	+	+	+	+	+	−
KCN --------	+	+	+	+	−	−
KCNS -------	+	+	+	+	−	−
$K_3Fe(CN)_6$ --	+	+	+	+	+	+
$K_4Fe(CN)_6$ --	+	+	+	+	+	+

The interfering influence of other constituents was then determined by taking once, twice, five and ten times the minimum amount of an anion that could be detected alone; in the presence of 200 mg. of each of the other anions. The following tables will show the effect of large quantities of other anions upon small amounts of an anion.

Behavior of KCl in Presence of 200 mg. of the Other Anions, Carried through the Scheme.

Amount in Presence of:	0.0 mg.	0.1 mg.	0.2 mg.	0.5 mg.	1 mg.
200 mg. KBr ------	−	+	+	+	+
" KI ------	−	+	+	+	+
" KCN ------	−	+	+	+	+
" KCNS -----	−	+	+	+	+
" $K_3Fe(CN)_6$-	−	+	+	+	+
" $K_4Fe(CN)_6$-	−	+	+	+	+

Behavior of KCNS in Presence of 200 mgs. of the Other Anions, Carried through the Scheme.

Amount in Presence of:	0.0 mg.	0.1 mg.	0.2 mg.	0,5 mg.	1 mg.
200 mg. KCl	–	+	+	+	+
" KBr	–	+	+	+	+
" KI	–	+	+	+	+
" KCN	–	+	+	+	+
" $K_3Fe(CN)_6$	–	+	+	+	+
" $K_4Fe(CN)_6$	–	+	+	+	+

Behavior of $K_3Fe(CN)_6$ in Presence of 200 mgs. of the Other Anions, carried through the Scheme.

Amount in Presence of:	0.0 mg.	0;1 mg.	0.2 mg.	0.5 mg.	1 mg.
200.mgs. KCl	–	+	+	+	+
" KBr	–	+	+	+	+
" KI	–	+	+	+	+
" KCN	–	+	+	+	+
" KCNS	–	+	+	+	+
" $K_4Fe(CN)_6$	–	+	+	+	+

Behavior of $K_4Fe(CN)_6$ in Presence of 200. mgs. of the Other Anions, Carried through the Scheme.

Amount in Presence of:	0.0 mg.	0.1 mg.	0.2 mg.	0.5 mg.	1 mg.
200 mgs. KCl	–	+	+	+	+
" KBr	–	+	+	+	+
" KI	–	+	+	+	+
" KCN	–	+	+	+	+
" KCNS	–	+	+	+	+
" $K_3Fe(CN)_6$	–	+	+	+	+

Behavior of KBr in Presence of 200 mgs. of the Other Anions, Carried through the Scheme.

Amount in Presence of:	0.0 mg.	0.1 mg.	0.2 mg.	0.5 mg.	1 mg.
200 mg. KCl	−	+	+	+	+
" KI	−	+	+	+	+
" KCN	−	+	+	+	+
" KCNS	−	+	+	+	+
" $K_3Fe(CN)_6$	−	+	+	+	+
" $K_4Fe(CN)_6$	−	+	+	+	+

Behavior of KI in Presence of 200 mgs.of the Other Anions, Carried through the Scheme.

Amount in Presence of:	0.0 mg.	0.1 mg.	0.2 mg.	0.5 mg.	1 mg.
200 mg. KCl	−	+	+	+	+
" KBr	−	+	+	+	+
" KCN	−	+	+	+	+
" KCNS	−	+	+	+	+
" $K_3Fe(CN)_6$	−	+	+	+	+
" $K_4Fe(CN)_6$	−	+	+	+	+

Behavior of KCN in Presence of 200 mgs. of the Other Anions, Carried through the Scheme.

Amount in Presence of:	0.0 mg.	0.1 mg.	0.2 mg.	0.5 mg.	1 mg.
200 mg. KCl	−	−	+	+	+
" KBr	−	−	+	+	+
" KI	−	−	+	+	+
" KCNS	−	−	+	+	+
" K Fe(CN)	−	−	+	+	+
" K Fe(CN)	−	−	+	+	+

Separation of the Anions of Group I.

	Ppt.		Sol.
1-2 cc. dilute HNO_3 Excess of $Zn(NO_3)_2$ 1-2 grams NH_4NO_3	$Zn_2Fe(CN)_6$	$Zn_3Fe(CN)_6$	$ZnCl_2$, $ZnBr_2$, ZnI_2, $Zn(CN)_2$, $Zn(CNS)_2$, ZnS.
10 cc. 10% NaOH 5-10 cc. 5% NH_4NO_3.	$Na_4Fe(CN)_6$, $Zn_2Fe(CN)_6$.	$Na_3Fe(CN)_6$ $Zn_3Fe(CN)_6$	
Confirmatory tests	$Cu_2Fe(CN)_6$ red. or $Fe_2(Fe(CN)_6)_3$ blue.	Oxidation of KI. or $Fe_3(Fe_2(CN)_6)_2$ blue.	
$AgNO_3$ excess Washed ppt.			$AgCl$., $AgBr$, AgI, $AgCN$, $AgCNS$, Ag_2S.

Treatment of Ag Precipitate containing Group I. still remaining.

1-2 grams $NaCO_2H$.				
5-10 drops N. KOH.	Ppt.		Sol.	
Vol. 10-20 cc.	AgI,	Ag_2S.	KCl, KBr, KCN, KCNS.	
0.2-1 gm. Zn.	ZnI,	ZnS		
Filter.				
1-2 drops HAc.				
1-2 drops $Tl(NO)_3$	TlI_3.			
	yellow			
1-2 drops HCl		H_2S		
PbAc paper		PbS		
		black	Ppt.	Sol.
Neutralize with H_2SO_4				
5-10 cc. H_2SO_3			CuCN. CuCNS	CuCl, CuBr.
Excess $CuSO_4$				

Ppt. | Sol.

5-10 drops N. KOH.
vol. 10 cc.

Confirmatory tests.

1/2 sol. for
each test.

$CuCN$ — KCN — $Fe_2(Fe(CN)_6)_3$ blue

$CuCNS$ — KCNS — $Fe(CNS)_3$ red

$CuCl$, $CuBr$. — Br — yellow color in CCl_4 layer.

$CuCl$ — $\underline{AgCl}$ white.

Boil sol. free from SO_2.

(reject ppt.)

1-2 cc. dil. H_2SO_4.

1 cc. 0.1 N. $KMnO_4$.

0.5-1 CCl_4.

Shake

15-20 cc. $KMnO_4$
boil 5-10 min.

filter.

Dil. filtrate to 50 cc.

1-2 cc. dil. HNO_3

1 drop N. $AgNO_3$.

IV. EXPERIMENTAL.

Stock solutions, cotaining varying quantities of each anion, as shown in table No. I, were made up for analysis. The scheme of analysis just outlined, was used through out. These solutions were labeled by an outside party, thus leaving the contents of each solution unknown. In the first analysis conducted, there were errors in manipulation, which resulted in the loss of the cyanide. The result of the first run of analyses is shown in table No. II. In every case, 50 cc. of the stock solution were taken for each analysis.

Table No. III. shows the results obtained by analysis,of the same solutions when all the proper precautions were taken. In practically every case it was possible to judge the amount of anion present from the amount of precipitate formed. Especially is this true of the ferricyanide,ferrocyanide, cyanide and thiocyanate whose precipitation is practically quantitative when the scheme is carefully followed.

STOCK SOLUTIONS.

mgs.	I	II	III	IIII	V	VI	VII	VIII
KCl ------	100	0	1	10	20	40	60	80
KBr ------	80	100	0	1	10	20	40	60
KI -------	60	80	100	0	1	10	20	40
KCN ------	40	60	80	100	0	1	10	20
KCNS -----	20	40	60	80	100	0	1	10
$K_3Fe(CN)_6$-	10	20	40	60	80	100	0	1
$K_4Fe(CN)_6$-	1	10	20	40	60	80	100	0
	A	C	E	G	H	F	D	B

FIRST TRIAL ANALYSIS.

	A	B	C	D	E	F	G	H
KCl	Pos.	Pos.	Neg.	Pos.	Pos.	Pos.	Neg.	Pos.
KBr	Pos.	Pos.	Pos.	Pos.	Neg.	Pos.	Pos.	Pos.
KI	Pos.	Pos.	Pos.	Pos.	Pos.	Pos,	Neg.	Pos.
KCN	Pos.	Neg.	Pos.	Neg.	Pos.	Neg.	Pos..	Neg.
KCNS	Pos.	Neg.	Pos.	Pos.	Pos.	Neg.	Pos.	Pos.
$K_3Fe(CN)_6$	Pos.	Pos.	Pos.	Neg .	Pos.	Pos.	Pos.	Pos.
$K_4Fe(CN)_6$	Pos.	Neg.	Pos.	Pos.	Pos.	Pos.	Pos.	Pos.

FINAL ANALYSES.

mgs.	A	B	C	D	E	F	G	H
KCl	Pos.	Pos.	Neg.	Pos.	Pos.	Pos.	Pos.	Pos.
KBr	Pos.	Pos.	Pos.	Pos.	Neg.	Pos.	Pos.	Pos.
KI	Pos.	Pos.	Pos.	Pos.	Pos.	Pos.	Neg.	Trace
KCN	Pos.	Pos.	Pos.	Pos.	Pos.	Neg.	Pos.	Neg.
KCNS	Pos.	Pos.	Pos.	Pos.	Pos.	Neg.	Pos.	Pos.
$K_3Fe(CN)_6$	Pos.	Pos..	Pos.	Neg.	Pos.	Pos.	Pos.	Pos.
$K_4Fe(CN)_6$	Pos.	Neg.	Pos.	Pos.	Pos.	Pos.	Pos.	Pos.

V. SUMMARY.

In this investigation a method of separation has been worked out, for those anions whose silver salts are insoluble in dilute nitric acid, but whose barium salts are soluble in water and acids. The ferricyanide and ferrocyanide are first precipitated as the zinc salts. The remaining anions are precipitated as the silver salts in an acid solution. The silver salts are reduced in an alkaline solution by sodium formate. This leaves the iodide and sulfide in the precipitate, from which the iodide is obtained through zinc reduction, while the sulfide test is obtained by acidifying. From the filtrate the cyanide and thiocyanate are precipitated as their cuprous salts. The precipitate is treated with dilute caustic alkali and the anions are dissolved while the copper is precipitated, thus avoiding the interfering action of copper. The chloride and bromide contained in the filtrate of the cuprous precipitation may be separated by oxidation with potassium permanganate, or any other commonly used method.

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